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ANION MOBILITY IN SOILS
Relevance to Nutrient Transport from Terrestrial to Aquatic Ecosystems

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PR-CC6991935-J

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory (CERL).

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes the influence of soil anion adsorption properties on the leaching of nutrients from soils and subsequent transport to streams. This work was undertaken as a part of a research program at CERL to determine the effects of acid rain on forest ecosystems.

A. F. Bartsch
Director, CERL

ABSTRACT

Nutrient transport from terrestrial to aquatic ecosystems is strongly mediated by soil chemical interactions. Ions deposited on or biologically released within the soils can enter into a variety of exchange and precipitation reactions prior to (or instead of) entering aquatic ecosystems. This report reviews the current knowledge of soil anion adsorption reactions and their effects on leaching, and suggests a simple model, based on anion production and adsorption considerations, to predict and explain nutrient transport. The relationship of this approach to that based on cation production and adsorption is discussed.

This report was submitted in fulfillment of Contract No. PR-CC6991995-J by Dr. Dale Johnson under the sponsorship of the U.S. Environmental Protection Agency; work was completed as of March 31, 1977.

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SECTION I

INTRODUCTION

Nutrient transport from terrestrial to aquatic ecosystems is strongly mediated by soil chemical interactions. Ions deposited on or biologically released within the soil can enter into a variety of exchange and precipitation reactions prior to (or instead of) entering aquatic ecosystems. If nutrient ions are precipitated or adsorbed to the soil, they cannot travel out of the terrestrial ecosystem via solution phase, that is nutrients cannot leach through the soil. Soil scientists have therefore had an intense interest in soil adsorption reactions and their effects on leaching for many decades. Historically, cation exchange reactions have been studied in great depth by soil scientists because most soils have a greater cation exchange capacity than an anion exchange capacity (Bear, 1955). Since cation exchange is far better known and better defined than anion exchange, there are many models available which describe cation exchange and cation movement through the soil (Biggar, et al. 1966; Carlson and Buchannan, 1973; and Butt and Tanji, 1982, to name only a few examples). Bolt (1967) gives an excellent review of cation exchange equations used in soil science and the theories behind them, and Reiniger and Bolt (1972) give an excellent discussion of the application of the theory of chromatography to cation exchange and leaching in soils. A brief summary of some aspects of cation exchange modeling is given in the Appendix, but no attempt will be made here to review the mass of literature on the subject. The reader is referred to the above papers for details.

While cation exchange models have proven useful in illuminating many aspects of cation exchange processes and in certain practical applications such as soil alkalinization and reclamation problems (Rible and Davis, 1955), there are simplifying assumptions inherent in each of them which render them inappropriate and perhaps useless for certain field applications. A major assumption in many of these models is that the exchanger (e.g., the soil) is unable to adsorb anions (Bolt, 1967), and it will be shown in this paper that this assumption renders cation exchange models absolutely useless in predicting soil leaching under many conditions.

It has been suggested that leaching in temperate forest soils is limited by a lack of anions that are mobile in the soil (McColl and Cole, 1968; Remezov, 1958). According to this concept, leaching cannot occur without an anion or anions to maintain electrochemical neutrality in soil solution, cation exchange reactions notwithstanding. According to the concept of McColl and Cole (1968) and Cole, et al. (1975) nutrient leaching occurs when H^+ or other non-nutrient cations are introduced to the soil with an anion that is mobile in the soil. If we adopt this view of leaching, we can couple

anion mobility considerations with erosion considerations and produce a simple conceptual picture of nutrient transport from terrestrial to aquatic ecosystems as shown in Figure 1. Though cation budgets are not considered in this picture, the total of cations must equal the total of anions, and one of the many cation exchange models could easily be introduced if one desired to consider individual cations. Paradoxically, it is in many ways easier to employ anion production and adsorption considerations to predict and explain nutrient transport than it is to consider cation production and adsorption, even though there is a far greater wealth of information on the latter. Also, in terms of pollution considerations, the nitrate and phosphate anions are of more interest than the major cations.

Thus, it is the intent of this paper to discuss the factors affecting anion mobility in soils, and to show how these factors in turn affect the rates of nutrient leaching from soils. To do this, we must first review the literature dealing with basic soil chemical reactions that are relevant to the level of anions in soil solution. Soil anion adsorption is important in this regard except in the case of bicarbonate. Thus, bicarbonate is discussed separately, and following that the mechanisms of anion adsorption are reviewed and related to field applications.

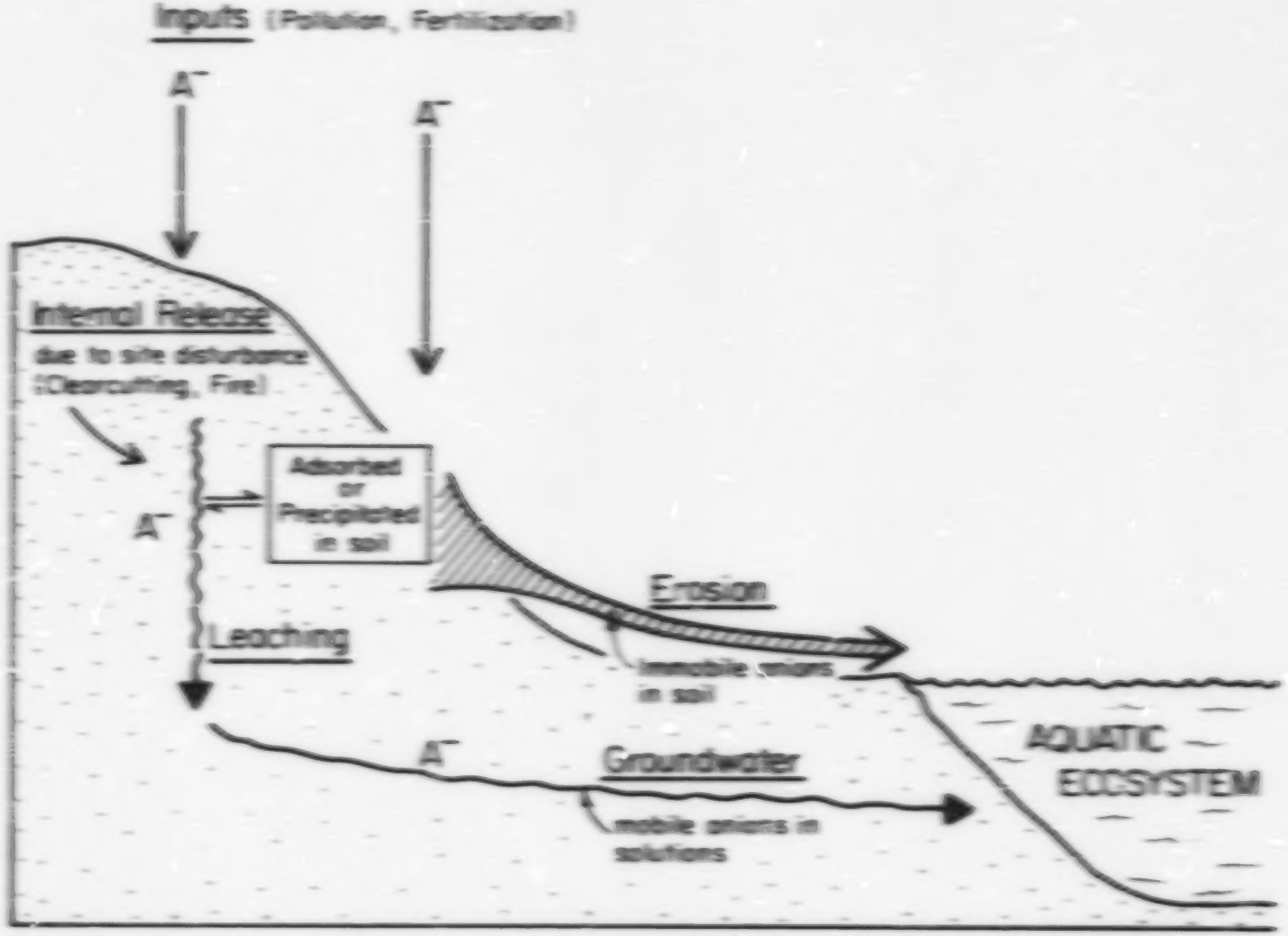

Figure 1. Conceptual scheme of toxic transport from terrestrial to aquatic ecosystems acting anion mobility as an index.

SECTION 2

FACTORS AFFECTING ANION PRODUCTION AND MOBILITY IN SOILS: A BRIEF LITERATURE REVIEW.

THE BICARBONATE ANION: A PRODUCT OF SOIL RESPIRATION

Factors Affecting the Concentration of Bicarbonate in Solution

Shilova (1959) and McColl and Cole (1968) showed that bicarbonate was the major anion in soil solutions from the temperate forest sites they investigated and they deduced that carbonic acid was the major soil leaching agent. Cole, et al. (1975) described the carbonic acid leaching mechanism as follows. Due to respiration and reduced CO_2 diffusivity in the soil, CO_2 pressure builds up within the soil relative to the ambient atmosphere. An incoming wetting front encounters this higher CO_2 pressure (and may increase it by further reducing CO_2 diffusivity) and CO_2 dissolves to form carbonic acid according to Henry's law:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$[H_2CO_3^*] = (Kh)(PCO_2) \qquad (1)$$

where Kh = Henry's law constant (= -1.46)

PCO_2 = CO_2 pressure in atmospheres

$[H_2CO_3^*] = [H_2CO_3] + [CO_2]aq$ (by convention)

Carbonic acid in turn dissociates to hydrogen and bicarbonate ions (or to carbonate at pH above 8.3):

$$H_2CO_3^* \rightarrow H^+ + HCO_3^-$$

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3^*]} = K_1 \qquad (2)$$

where K_1 = the first dissociation constant of carbonic acid.

Following this, hydrogen-cation exchange occurs and a bicarbonate salt leaves the system. The scheme of events associated with this mechanism is shown in Figure 2.

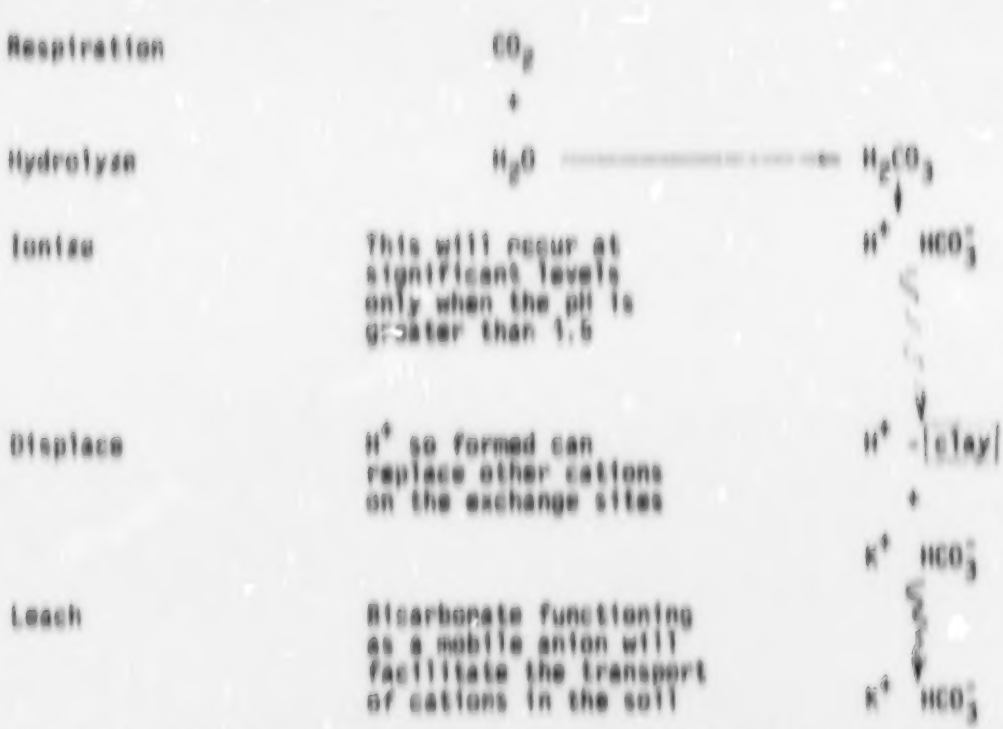

Figure 2. Schematic diagram of events associated with carbonic acid leaching in soils (From Cole, et al., 1975).

Following equation (1) and (2), it is easily seen that the concentration of bicarbonate is determined by CO_2 pressure (PCO_2) and pH ($\{H^+\}$):

$$[HCO_3^-] = \frac{(K_1)(Kh)(PCO_2)}{[H^+]} \qquad (3)$$

The response of bicarbonate to changes in pH and PCO_2 is shown in Figure 3. Thus, we see that the rate of soil leaching by carbonic acid is regulated by soil respiration, soil CO_2 diffusivity (which is also determined by rainfall intensity), and final solution pH. CO_2 pressure may be thought of as a potential for carbonic acid leaching, and the extent to which this potential is realized is determined by solution pH.

Soil Properties in Relation to Solution Bicarbonate Levels

In rapidly respiring, finely porous soil, CO_2 pressure and carbonic acid leaching potential will be high. Also, CO_2 can build up to high pressures beneath impermeable ice or snow layers even though respiration is low (Markarov, 1966).

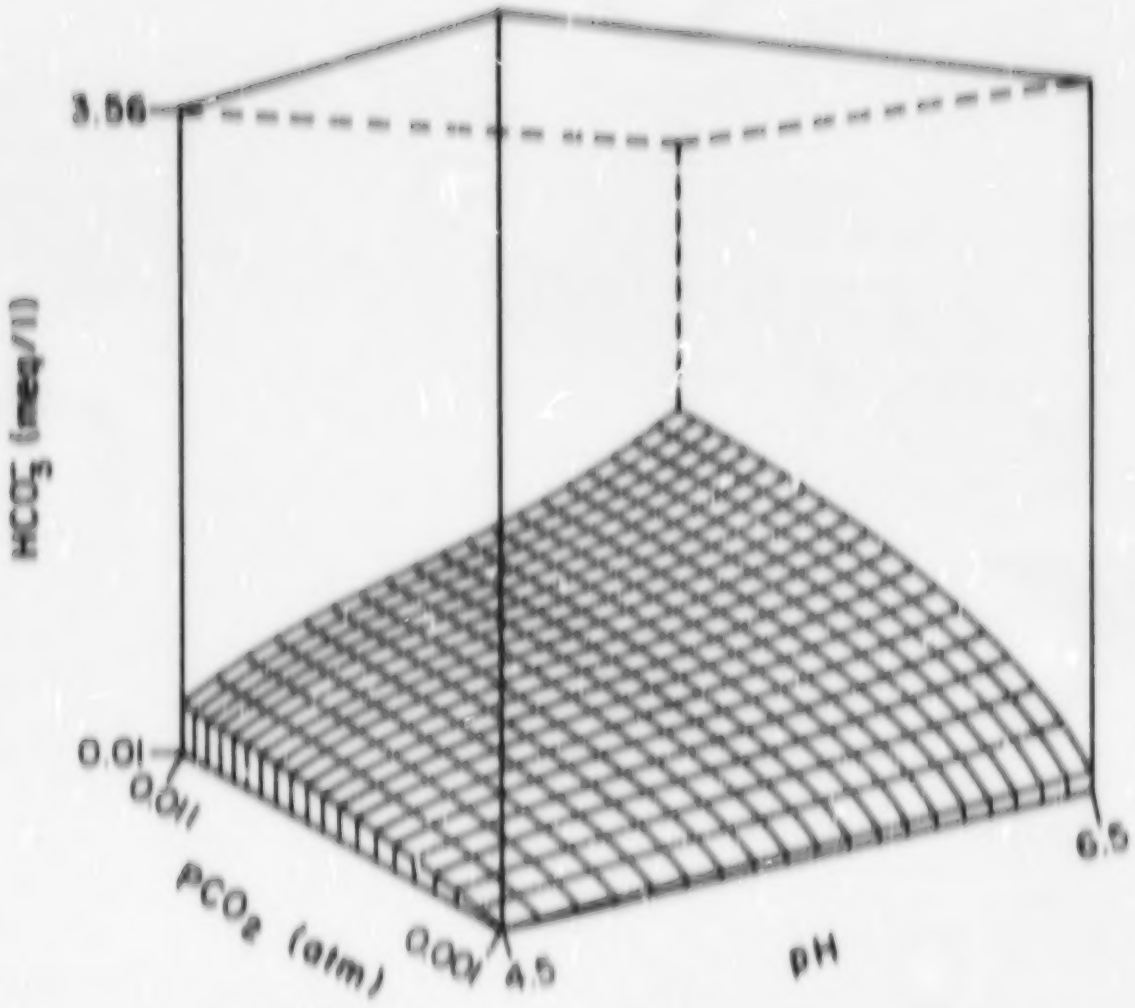

Figure 3. Response of HCO_3^- to changes in pH and CO_2 pressure (PCO_2)

Factors affecting pH are more complex. Soil solution pH can be affected by percent base saturation, low base soils giving lower pH than high base soils (Schofield, 1947). In cold-region podzols, however, organic acids are typically present and they buffer solution pH at low levels (Strelkova, 1974); Ponomareva et al., 1968; Ponomareva, 1973).

The senior author investigated soil leaching processes in forests growing under a variety of climatic conditions, and found that the importance of carbonic acid leaching decreased as annual temperature decreased (Johnson, 1975). In the tropical soil, high soil respiration and low soil CO_2 diffusivity led to high soil CO_2 pressures which in turn led to intense carbonic acid leaching. The temperate forest soil was also leached primarily by carbonic acid, but at a less intense rate than the tropical soil due to lower soil CO_2 pressure. Organic acids were present in solutions from the subalpine and northern soils, and they lowered solution pH to levels such that carbonic acid played a minor or nonexistant role in leaching these soils,(i.e., solution pH was so low that carbonic acid did not dissociate into H^+ and HCO_3^-). Organic acids were found to be similarly important in solutions from cold-region podzols in the Soviet Union as well (Ponomareva, et al, 1968; Ponomareva, 1973).

Some Examples of Bicarbonate Leaching in Response to Site Manipulation

From the previous discussion, it is clear that any site manipulation that affects soil CO_2 pressure or solution pH will affect solution bicarbonate levels. In practice, solution pH is the more important of the two factors, since a change of one pH unit causes a change of ten-fold in solution bicarbonate concentration.

Cole, et al. (1975) give an excellent review of the effects of urea fertilization, harvesting and fire on bicarbonate leaching in a Douglas fir forest soil. In terms of harvesting, the input of foliage and branches to the forest floor compartment dramatically increases the nutrient content of that compartment. This, coupled with an increase in surface temperature, leads to a rapid acceleration in the decomposition rate (Gessel and Cole, 1965). This was because the more acid lower soil horizons donated hydrogen ions to solution, reducing bicarbonate concentration and causing associated cations to occupy exchange sites. These reactions are depicted in Figure 4.

Burning slash after clearcutting obviously alters the chemical nature of the forest floor nutrient pool; it is, in essence, an instantaneous decomposition of the organic material as opposed to the slower, biological process. Burning results in substantial volatilization of nitrogen and sulfur conversion of non-volatitic minerals to oxides. The oxides soon convert to highly soluble carbonates which remain in the ash layer until they are leached. With the onset of precipitation, carbonates (CO_3^-) dissolve and consume hydrogen ions from exchange sites to form metal bicarbonates ($X^+HCO_3^-$) (Figure 4). With massive fluxes of these species, the soils buffering capacity is exceeded and the result is significant increases in cation-bicarbonate concentrations in solutions below the rooting zone. Even so, however, 70-90% of the cations mobilized from the ash layer remained within the rooting zone. A loss of 10-30% of the cation mineral reserve in the forest floor and foliage is worthy

of consideration, but the loss by volatilization of 90% of the nitrogen in those components is by far the most serious concern (Grier, 1975).

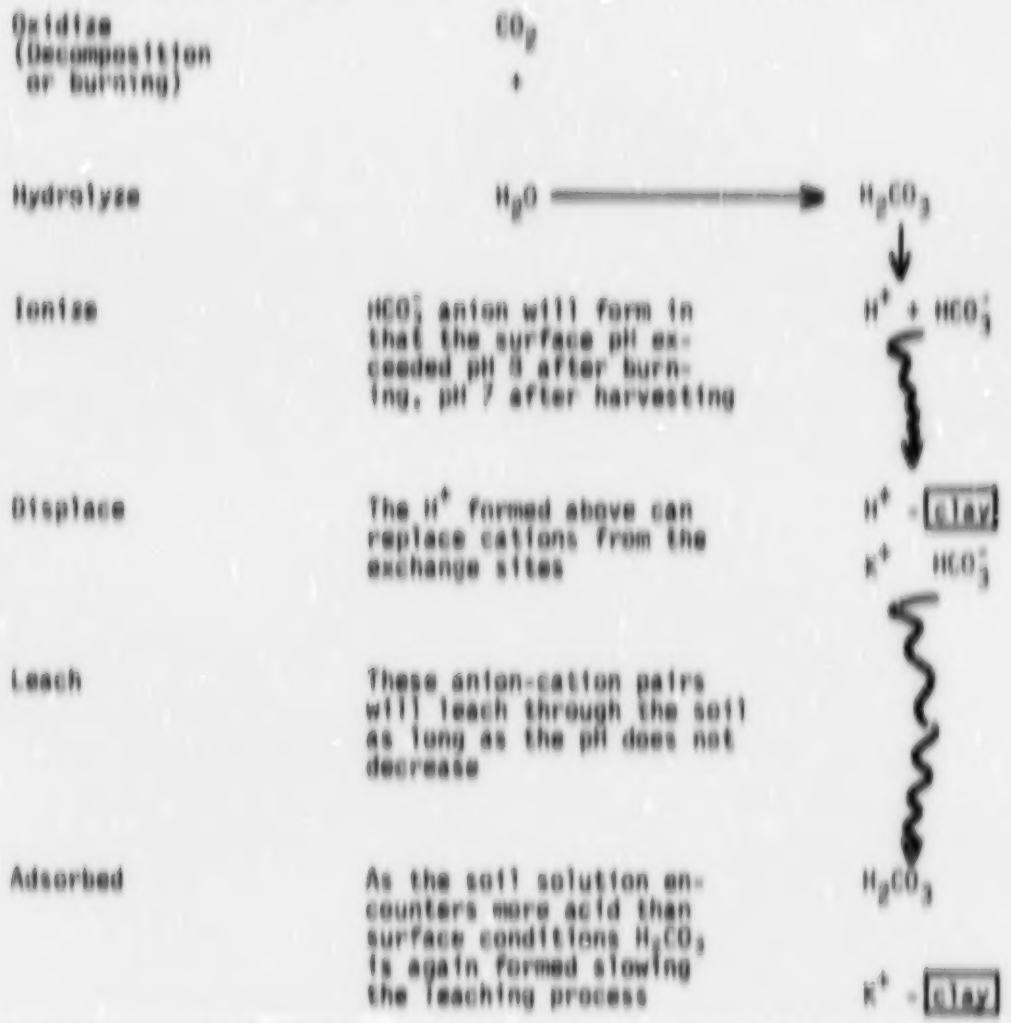
Oxidize (Decomposition or burning)
CO_2
Hydrolyze
H_2O
H_2CO_3
Ionize
HCO_3^- anion will form in that the surface pH exceeded pH 8 after burning, pH 7 after harvesting
$H^+ + HCO_3^-$
Displace
The H^+ formed above can replace cations from the exchange sites
H^+ - clay
K^+ HCO_3^-
Leach
These anion-cation pairs will leach through the soil as long as the pH does not decrease
Adsorbed
As the soil solution encounters more acid than surface conditions H_2CO_3 is again formed slowing the leaching process
H_2CO_3
K^+ - clay

Figure 4. Schematic diagram of bicarbonate leaching following harvesting or burning (from Cole, et al., 1975).

Urea fertilization has profound effects on the amount of cation transfer in upper soil horizons as well. Urea is a highly soluble non-ionic polar organic compound, and it is therefore readily leached if applied during rainy periods. However, urea hydrolyzes to ammonia and carbon dioxide through an enzymatic reaction involving urease. (Urease is commonly present in forest soils). NH_3 then consumes hydrogen ions to form NH_4^+ and CO_2 hydrolyzes to form carbonic acid which in turn dissociates into H^+ and HCO_3^-, dependent upon pH. Since carbonic acid is a weakly dissociated acid and there are two NH_3 molecules produced for each CO_2, the net result is a sharp rise in solution pH. In most cases HCO_3^- remains the dominant carbonate form (pH remains below

8.3), so that an ammonium bicarbonate solution results. (This must result in the initial transfer of NH_4^+ to exchange sites in order to maintain mass balance). As the ammonium bicarbonate solution moves through the soil profile, NH_4^+ displaces native cations such as K^+, Ca^{++}, Mg^{++}, and H^+ from the exchange sites by mass action (Figure 5). Thus, urea fertilization makes many cation nutrients available for uptake in addition to NH_4^+. Displaced H^+ combines with HCO_3^- to form H_2CO_3, so that bicarbonate concentrations as well as ammonium concentrations decrease as solutions pass deeper into the soil. The result is that NH_4^+ is largely retained in the upper 15 cm of the soil. Should the initial hydrolysis of urea be delayed or blocked, far greater leaching losses of N would occur. In most cases the hydrolysis is rapid enough so that little N loss occurs, however.

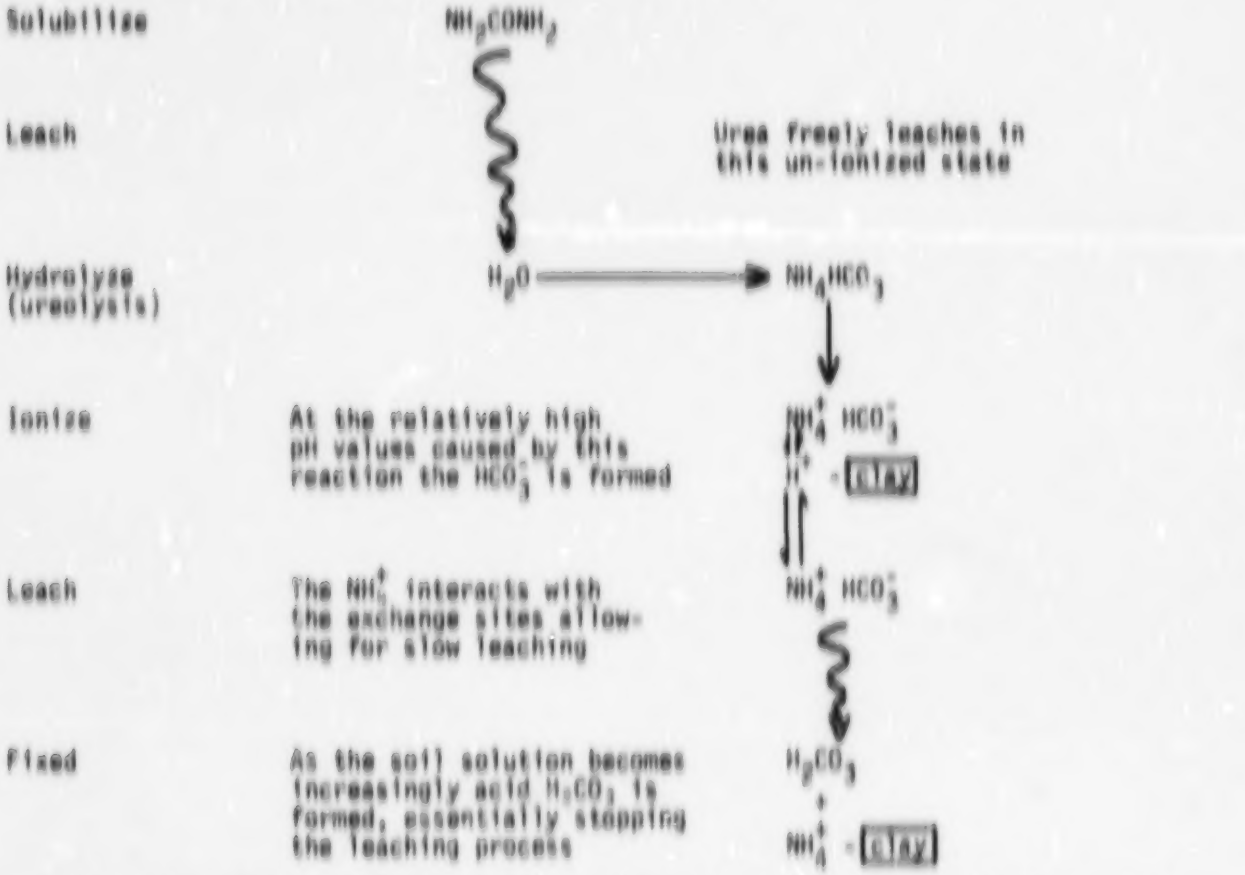

Figure 5. Schematic diagram of transformation and leaching of urea within the soil profile (Cole et al., 1975).

For reasons unknown, nitrification did not occur following urea fertilization. This is fortunate in terms of N retention, in that NO_3^- is a relatively mobile anion in the soil and would readily leach out.

In soil where bicarbonate is normally absent, one would expect urea fertilization to have a more dramatic effect on soil leaching than in soils where bicarbonate is normally dominant. This author (Johnson, unpublished data) tested the effect of urea fertilizer on bicarbonate leaching in a subalpine ecosystem where bicarbonate is normally unimportant through most of the soil, and it was found that annual leaching rates increased by a factor of 7 in the upper 15 cm and by a factor of almost 2 in the 60 cm level. This was a greater increase than that noted by Crane (1972) after similar urea applications on a bicarbonate-dominated soil.

NITRATE, CHLORIDE, SULFIDE, AND PHOSPHATE LEACHING IN SOILS

Aside from bicarbonate and organic anions, sulfate, chloride, nitrate and phosphate deserve careful consideration in terms of soil leaching. Chloride is an important anion in soil solutions near coastal areas (Art, et al., 1974; Johnson, 1975), and it is quite mobile in the soil. Like carbonic acid production, the microbiological conversion of ammonium to nitrate, or nitrification, produces both H^+ and a mobile anion (NO_3^-), thus allowing a very effective leaching process. Likens, et al. (1969) showed clearly the importance of nitrate to forest soil leaching following clearcutting in the Hubbard Brook watershed, and Cole, et al (1975) show the importance of this anion to leaching following wastewater application in western Washington.

Oxidation of sulfur in soils produces H^+ and sulfate ($SO_4^{=}$) (Reuss, 1975), but field application of sulfuric acid to forest soils have led only to small increases in leaching in western Washington (Johnson and Cole, 1976) and in Norway (Abrahamsen, et al., 1975). In the Washington case, we showed that sulfate adsorbed strongly to the soil and therefore leaching was greatly restricted.

Phosphate (as well as the other anions discussed above) is commonly applied in fertilizers. Fortunately phosphate adsorbs even more strongly to soils than sulfate does, and in addition, it is immobilized by a variety of precipitation reactions that are discussed later in this paper. Consequently, changes of phosphate leaching through a soil profile are very much less than those of sulfate, and changes of sulfate leaching are very much less than those of nitrate due to soil adsorption properties.

With the exception of bicarbonate (which, as has been discussed, is primarily regulated by CO_2 pressure and pH), soil anion adsorption can exert a tremendous influence on the concentration of anions in soil solution and consequently on the leaching processes within the soil. It is therefore appropriate at this point to review some of the literature dealing with the basic mechanisms of anion adsorption in soils. Following that, some examples can be drawn from the literature as well as elsewhere to show the importance of anion adsorption to the transport of nutrients through the soil.

Adsorption Mechanisms

Anion adsorption is normally associated with oxides or hydrous oxides of iron and aluminum, though kaolinite is known to be an absorber to a lesser extent (Mekaru and Uehara, 1972; Gebhardt and Coleman, 1974; Alymore, et al, 1967; Hingston, et al., 1967; Chao, et al., 1964). Basically, there appear to be two mechanisms of adsorption: 1) non-specific, in which anions are held as counter-ions in the diffuse double layer next to a positively charged colloidal surface, and 2) specific, in which anions enter into coordination with metal oxide (i.e., they become bonded to two or more ions in the crystal structure) and they displace another anion. The latter is sometimes called ligand exchange (Mekaru and Uehara, 1972; Hingston, et al., 1967).

The difference between the two types of adsorption is as follows. Sites for non-specific adsorption lie on the surfaces of colloids, and these surfaces can have a plus, minus, or zero charge depending on the concentration of potential determining ions. For sesquioxides, the potential determining ions are usually H^+ and OH^-; thus, surface charge is pH-dependent. At low pH (high H^+ concentration) surfaces become positively charged because of H^+ adsorption, whereas at high pH (low H^+ concentration) become negatively charged because of H^+ dissociation (or OH^- adsorption), as shown in Figure 6 (Hingston, et al., 1967; Harward and Reisenauer, 1966; Yopps and Fuerstenau, 1964). The pH at which the surface has no charge is termed the zero point of charge (ZPC). The ZPC of iron and aluminum oxides common in soils lies in the vicinity of pH 9, thus, these surfaces have a net positive charge at most normal soil pH's, and they provide sites for anion adsorption (Hingston, et al., 1967; Yopps and Fuerstenau, 1964; Harward and Reisenauer, 1966). If pH is lowered in a given soil, these surfaces become more positively charged and anion adsorption increases, whereas if pH is raised, these surfaces become less positively charged or negatively charged, and anion adsorption decreases.

All major anions are involved in non-specific adsorption, but not all anions enter into specific adsorption reactions. Cl^- and NO_3^- are termed "indifferent" anions because they do not specifically adsorb and they can be completely desorbed by eliminating the positive charge on colloidal surfaces (e.g., by raising pH) (Hingston, et al., 1967; Mekaru and Uehara, 1972).

On the other hand, anions like sulfate and phosphate (also selenite, silicate, and fluoride) enter into specific adsorption as well as non-specific adsorption reactions. Hingston, et al. (1967) describe the nature of specific adsorption in great detail, but only a few major points will be discussed here. Phosphate always adsorbs more strongly than sulfate on a given soil, and phosphate will displace adsorbed sulfate as well as nitrate and chloride (Harward and Reisenauer, 1966). Donnan equilibrium equations apparently do not apply, however, since sulfate will not displace phosphate, and in some cases phosphate will not displace all adsorbed sulfate (Bornemisza and Llanos, 1967; Harward and Reisenauer, 1966). In general, the displacing or adsorbing capacity of major anions are as follows: $PO_4^{3-} > SO_4^{2-} > Cl^- = NO_3^-$. Recall that the latter two are non-specifically adsorbed. Specific adsorption of PO_4^{3-} or SO_4^{2-} can result in increased negative charge (or less positive charge) on colloids, and this is the primary means by which non-specifically adsorbed anions are displaced by specifically adsorbed anions (Mekaru and Uehara,

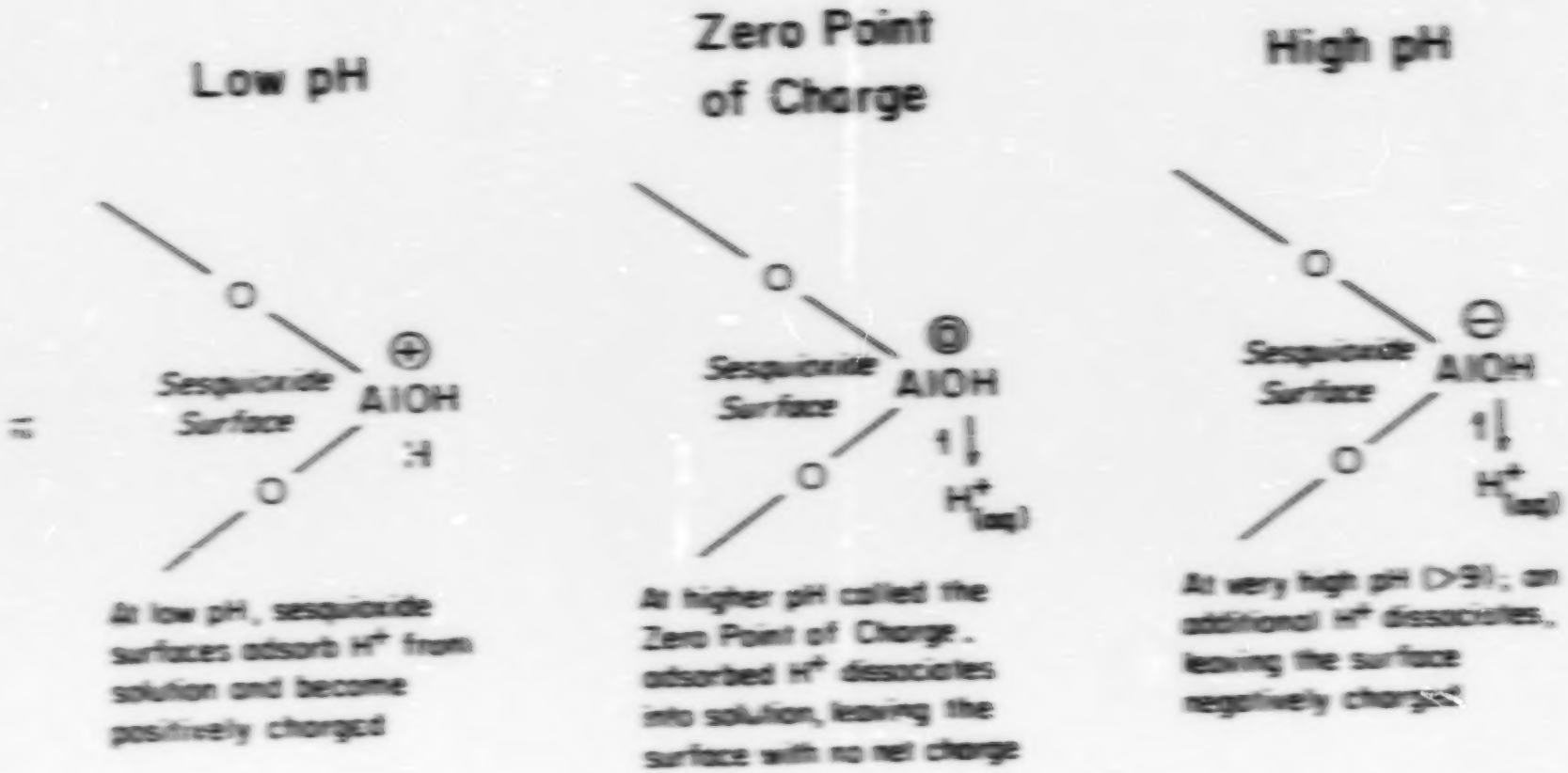
Low pH
Zero Point of Charge
High pH
Sesquioxide Surface
AlOH
At low pH, sesquioxide surfaces absorb H+ from solution and become positively charged
At higher pH called the Zero Point of Charge, absorbed H+ dissociates into solution, leaving the surface with no net charge
At very high pH (>9), an additional H+ dissociates, leaving the surface negatively charged

Figure 6. Schematic representation of the effect of pH on surface charge of sesquioxides

1972; Hingston, et al., 1967). This increased negative charge naturally must lead to an increase in cation exchange capacity as well (Mekaru and Uehara, 1972). Thus, in a soil that is subjected to heavy applications of sulfate or phosphate, one would expect to see the release of whatever Cl^- or NO_3^- that was non-specifically adsorbed to the soil (if any). As many examples will show in the next section, however, little cation loss occurs with heavy applications of sulfate and phosphate despite the possibility of this "anion exchange" with chloride or nitrate, probably because of low initial levels of adsorbed chloride and nitrate relative to the incoming sulfate or phosphate. The increased cation exchange capacity with sulfate or phosphate adsorption undoubtedly helps retain the applied cations also.

Phosphate undergoes immobilization reactions other than adsorption, also. It readily precipitates with Al, Ca, Mg, and other common cations in soil solution and can eventually form new minerals such as variscite ($AlPO_4 \cdot 2H_2O$), fluorapatite ($Ca_{10}(PO_4)_6(OH)_2$), and strengite ($FePO_4 \cdot 2H_2O$), among others (Lindsay and Moreno, 1960; Hsu and Jackson, 1960). There is evidence that adsorbed or precipitated phosphate becomes "fixed" into mineral forms and less easily desorbed with time and wetting and drying cycles (Lindsay and Moreno, 1960; Sawhney and Hill, 1975). Thus, it seems safe to assume that almost all soils (including calcareous) will strongly adsorb or otherwise immobilize phosphate.

Of the major anions present in natural waters, only bicarbonate has been left out of the discussion of anion adsorption. To the best of this author's knowledge, no information is available as to the absorptivity of the bicarbonate anion. This is probably due to experimental difficulties in keeping material balance for the bicarbonate anion, since it is in equilibrium with atmospheric CO_2 in the soil, and it is so strongly affected by pH. For these same reasons, however, it seems likely that soil CO_2 pressure and soil solution pH are far more important to the mobility of the bicarbonate anion than soil adsorption is.

Soil Properties in Relation to Anion Adsorption

With the information summarized in the previous section, we can begin to make some basic predictions as to the susceptibility of soils to leaching. It is clear, for instance, that sesquioxide-rich soils like lateritic soils will be more efficient anion adsorbers and thus allow less leaching than sesquioxide-poor soils like those derived from granite. It is also clear that for a given soil, applications of phosphate salts or acids will result in less leaching than applications of sulfate salts or acids, and applications of nitrate or chloride salts or acids will result in the most leaching. A few specific examples of these relationships will now be given.

Early work by Chao, et al. (1962) in Oregon soils showed that of the 16 soils investigated, only two latosols, one reddish-brown lateritic soil, and one andept adsorbed sulfate to any significant extent. Later the same authors (Chao, et al., 1964) demonstrated good relationships between iron and aluminum coatings and sulfate adsorption in soils from Oregon.

Barrow, et al. (1969) found a strong correlation between amount of rainfall and soil sulfate adsorption capacity. They hypothesized soils in higher rainfall areas had higher aluminum and iron oxide contents, which in turn gave them higher sulfate adsorption capacities. These authors also noted that soils derived from siliceous rocks such as granite and shale had less sulfate adsorption capacity than those derived from basalt, as one would expect by the generally lower aluminum content in the former.

Bornemisza and Llanos (1967) measured sulfate adsorption on a Latosol, a volcanic soil, and an alluvial soil from Costa Rica, and they found sulfate adsorption to be greatest in the Latosols, less in the volcanic soil, and least in the alluvial soil, as one would expect from the relative sesquioxide contents. The differences they reported were large, ranging from 50 to 90% using the Latosol as a baseline.

This author (Johnson and Cole, 1976; Johnson, 1976; and unpublished data) has measured sulfate, phosphate, nitrate, and chloride adsorption isotherms for the Everett soil, a gravelly outwash from western Washington. The interest here was in relating these isotherms to soil solution properties in the field, and consequently the concentration values employed were much lower than those reported in previous literature. As a result of this difference in scale, there are few points at which these isotherms can be compared to those determined for other soils. In the case of nitrate, however, a clear comparison can be made: no nitrate adsorption was observed for the Everett soil, whereas Kinjo and Pratt (1971) measured significant nitrate adsorption in Andepts and Oxisols from Central and South America. The authors note that these soils are especially rich in amorphous iron and aluminum and that little or no nitrate adsorption would be expected in most temperate soils. Gebhardt and Coleman (1974) measured anion adsorption on some Andepts from Hawaii, Mexico and Columbia for a solution concentration of 5 meq/l, so that some comparisons between the Everett soil and the Andepts are possible. The Everett soil retains 0.3 meq/100g of Cl^- and the Andept retains about 1 meq/100g of Cl^- at this solution level, and the values for sulfate are 0.8 and 2, respectively. Clearly, the Andept retains these anions better than the gravelly Everett soil. A better comparison can be made between the Everett soil and the Bohannon soil which is being used for part of EPA's acid rainfall studies. The latter is a finer textured, older and more weathered soil derived from sandstone, and consequently it probably has a higher sesquioxide content than the Everett soil. The very fact that it is finer textured than the Everett may lend it greater adsorbing capacity, also, but it is clear from the comparison in Figure 7 that it does indeed have a greater adsorption capacity at a given solution level than the Everett does. Between concentrations of 0 and 0.2 meq/l the Everett appears to have a greater capacity, but in all probability this is due to the extraction methods used to get initial soil sulfate levels. Potassium phosphate was used to extract the Everett soil, whereas potassium chloride was used to extract the Bohannon soil, and the latter is a much weaker extractant than the former (Harward and Reisenauer, 1966).

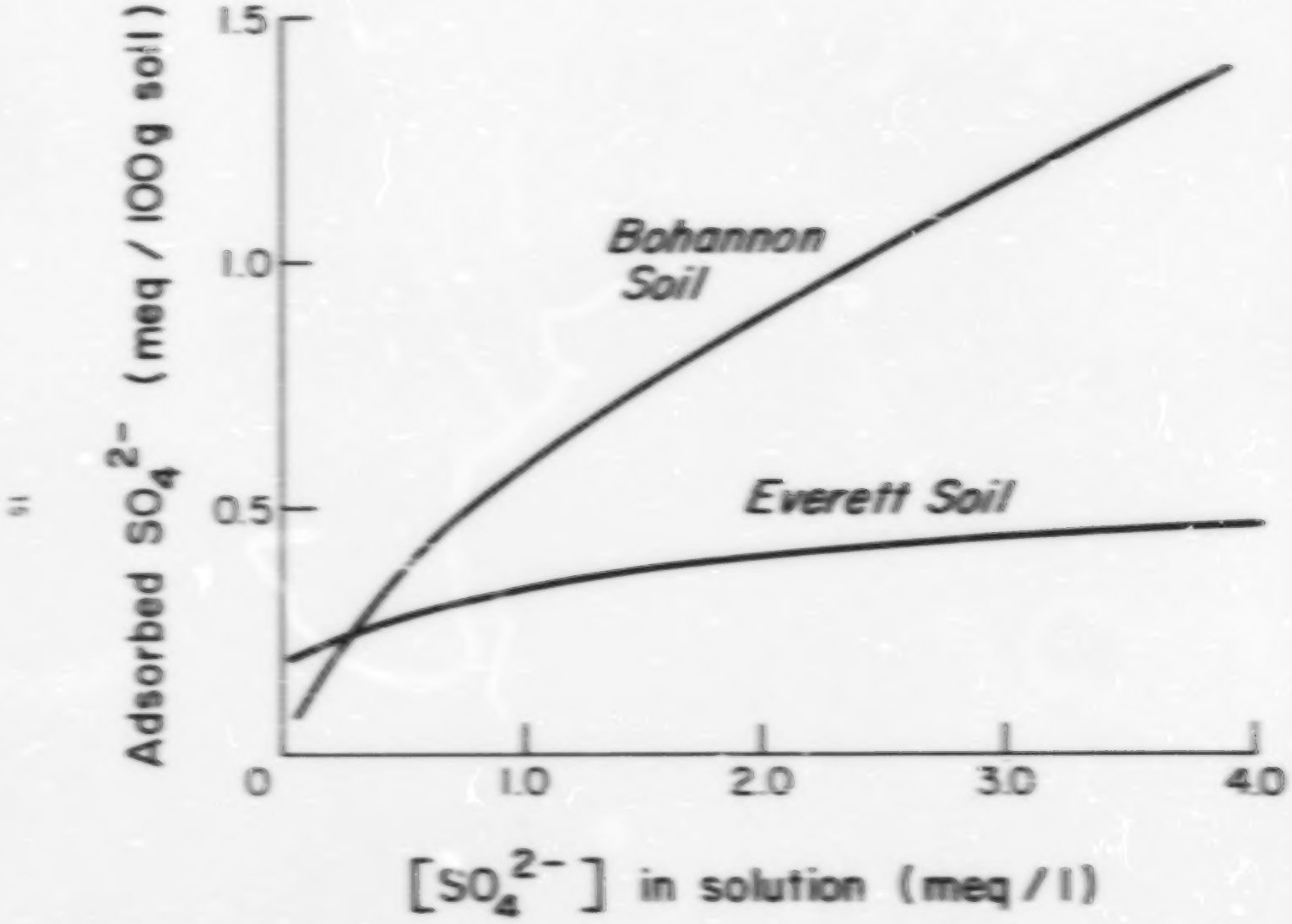

Figure 7. Comparison of sulfate adsorption isotherms for the Everett and Bohannon soils

Some Examples of Nitrate, Chloride, Sulfate and Phosphate Leaching in Response to Site Manipulations

An example of the great importance of anion mobility is given by Mekaru and Uehara (1972) in their excellent paper on anion adsorption in tropical soils. They cite the results of Ayres and Hagihara (1953), who applied potassium fertilizer to ferruginous tropical soils as salts of chloride, sulfate, and phosphate. Naturally, potassium added as KCl leached rapidly away compared to potassium added as sulfate or phosphate. Since sulfate and phosphate enter into specific adsorption reactions, addition of these salts of potassium should result in not only retention of the anions, but also an increase in cation exchange capacity which can in turn retain the added potassium. Thus, as this example shows, the anion associated with cation fertilizers is of the utmost importance and cannot be chosen at random.

Further examples of the importance of anion mobility to fertilizer application come from the studies conducted by Overrein (1971) in Norway. He describes the leaching of nitrogen applied in various forms to forest soils. He found that the NH_4 form was far less mobile than the NO_3 form of N, as one would expect. He also found that NH_4 leached farther into the soil when ammonium chloride was applied than when urea was applied. Once again, the mobility of the anion, Cl^- in this case, strongly affects the mobility to applied cations. Nitrogen applied as urea converts to ammonium bicarbonate, and the concentration of bicarbonate is regulated by soil atmospheric CO_2 and solution pH as previously discussed. Thus, though bicarbonate may be poorly adsorbed to soil, it can escape to the atmosphere and is not conserved as other anions are. As a result of this, urea is known to be retained strongly within forest soils (Roberge and Knowles, 1966; Crane, 1972; Cole, et al., 1975; Overrein, 1971).

The mobility of sulfate in soils is an important consideration in evaluating the possible effect of pollution-caused acid rain on nutrient transport from the soil. It cannot be assumed that inputs of sulfuric acid will result in equivalent outputs of cation-sulfate solutions from the soil, as was demonstrated in a simple experiment we performed on the gravelly Everett soil (Johnson and Cole, 1976). To test the mobility of sulfate in the soil, sulfuric acid was applied to the experimental plot at concentrations ranging from 10 to 1000 stronger than that normally occurring in precipitation (Johnson and Cole, 1976). Results showed that significant increases in leaching occurred in the forest floor and A horizon (12 cm deep in the soil), but no increase was noted in the B horizon (50 cm deep). Soil analyses revealed that all of the applied sulfate was retained within the soil profile.

Using the sulfate adsorption isotherm measured for the Everett soil (Figure 7), it is possible to calculate the sulfate concentration at any point in the soil profile given the value for the sulfate adsorbed to the soil. Given the flux of water, it is then possible to calculate the leaching of sulfate from any point in the profile to the next point in the profile. Finally, for any given point in the profile, the pool of adsorbed sulfate can be updated by adding the sulfate leaching in and subtracting the sulfate leaching out, and new solution sulfate concentrations in solution can then be calculated for the next leaching. Using this simple approach, a finite

difference model was constructed for the Everett soil, and the sulfuric acid applications described above were simulated (Johnson, 1975). The model also incorporated the bicarbonate equilibrium equations described previously and a cation exchange equation to account for hydrogen-cation exchange. Full details and results are given in Johnson (1975). For the purposes of this discussion, it is useful to compare the simulated and actual fluxes of sulfate and the final value of soil adsorbed sulfate (Table 1). It is obvious that the model overestimated the flux and underestimated the final soil adsorbed sulfate in the A horizon, whereas it overestimated the soil adsorbed sulfate in the B horizon. This result indicates that the assumption of complete reversibility of soil sulfate adsorption is in error; the A horizon retained more adsorbed sulfate in the B horizon than it would have if the adsorption reaction were completely reversible. Thus, it appears that both adsorption and desorption isotherms must be employed in efforts to predict the leaching of sulfate (or phosphate) in a given soil.

TABLE 1. MEASURED AND MODELED SULFATE FLUX AND SOIL SULFATE CONCENTRATION AFTER ACID APPLICATION (adapted from Johnson and Cole, 1976, and Johnson, 1975)

Horizon	Flux (equivalents/ha)		Soil sulfate meq/100g)	
	Measured	Modeled	Measured	Modeled
A	15000	32000	0.74	0.30
B	200	150	0.80	1.10

Also, if other anions are introduced into the system, the interactions between them must be determined and incorporated as well. The importance of these interactions is implied in the results of sulfuric acid application to forest soils in Norway. Abrahamsen, et al. (1975) noted a four-fold increase in cation leaching as a result of acid application, yet the increase is not balanced by increases in sulfate leaching (Tveten, et al., in press). Since the leachates must maintain electrochemical neutrality, the increased cation leaching must be balanced by increases in the level of an anion other than sulfate, and this in turn suggests that some form of "anion exchange" is taking place

Some further examples from the Everett soil can illustrate the relative mobilities of some major anions. Phosphate, sulfate, chloride, and nitrate adsorption isotherms for the Everett soil are shown in Figure 6. No nitrate adsorption occurred, and consequently the nitrate adsorption isotherm is a horizontal line starting at 0 on the Y-axis (i.e., it is identical with the X-axis line).

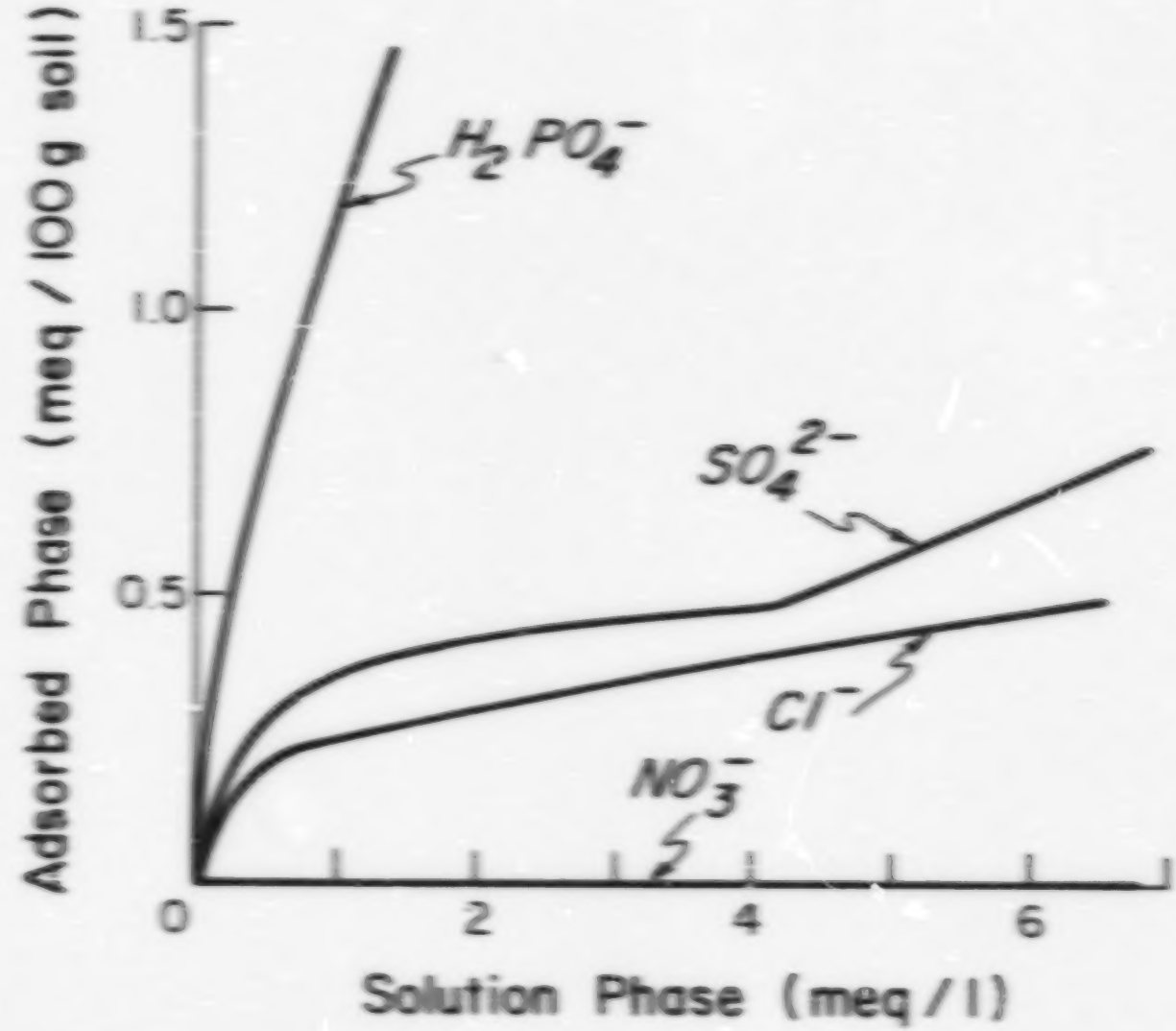

Figure 8. Absorption isotherms for chloride, sulfate, nitrate and phosphate on the Everett soil A-horizon

The relative adsorptivities of these anions as plotted here have also been reflected in field results from the application of sulfuric acid and wastewater to the Everett soil. In the case of sulfuric acid application, the significant increase in leaching in the A horizon (Table 1) suggests that the sulfate adsorption capacity of this horizon was being reached. On the other hand, over 500 kg/ha of phosphate has been applied to the same soil series in ongoing wastewater studies under the supervision of Dr. Dale Cole, while less than a fraction of a percent of this amount has leached past the 10 cm soil depth (Cole, 1976). At the other extreme of the adsorptivity scale, only about 30 kg/ha of nitrate has been applied in the same study, while over 100 kg/ha has leached past the 200 cm depth in the soil, presumably because of nitrification within the soil profile (Cole, et al., 1976). We are now sampling the soils from the irrigation plots and we fully expect that the final budgets will reflect the relative mobilities of these major anions in the soil.

SECTION 3

SUMMARY AND CONCLUSIONS

1. Anion production and leaching can be used effectively as an index of total ionic leaching through soils.

2. An anion of major importance in many soil solutions is bicarbonate, and the rate of bicarbonate leaching is regulated by soil CO_2 pressure and solution pH.

3. Anion adsorption is a very important feature of soils in terms of regulating the leaching rates of anions other than bicarbonate. In general, the order of affinities of major anions is $PO_4^{3-} > SO_4^{2-} > Cl^- = NO_3^-$. The first two anions can be adsorbed non-specifically and specifically whereas the latter two can only be adsorbed non-specifically. Specific adsorption refers to penetration of the anion into the coordination sphere of metal oxides, and non-specific adsorption refers to anion retention in the diffuse double layer next to oxide surfaces. Bicarbonate adsorption has not been well characterized, but it is exceptional in that it is regulated primarily by soil CO_2 pressure and solution pH.

4. The anion adsorption capacity of a soil is related to the content of positively charged sesquioxides in the soil. Highly-weathered, iron and aluminum-rich soils have higher adsorption capacities than younger iron and aluminum-poor soils.

5. For a given soil:

   a) Changes in pH will affect bicarbonate concentrations and anion adsorptivity and therefore leaching rates. Such changes affect non-specific adsorption in that sesquioxide surfaces lose H^+ and net positive charge as pH increases. Bicarbonate concentration also increases as pH increases. Consequently, increases in pH will mobilize non-specifically adsorbed anions and bicarbonate and tend to increase leaching rates.

   b) The addition of specifically adsorbed anions to a soil will result in the mobilization of non-specifically adsorbed anions. This occurs because the specific adsorption of anions increases the permanent negative charge of sesquioxide surfaces. The latter also results in increased cation exchange capacity and greater cation retention power. Phosphate is the most strongly adsorbed anion and will displace specifically adsorbed sulfate as well as non-specifically adsorbed anions.

6. In general, it is clear that the concept of anion mobility in soils is a very useful tool for predicting the effects of site manipulations such as fertilization, harvesting, burning, and wastewater application on soil leaching rates. In considering terrestrial-to-aquatic nutrient transport, it is critically important to consider the factors affecting the addition, production and mobility of anions in the soil.

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APPENDIX

A BRIEF SUMMARY OF SOME APPROACHES USED IN MODELING CATION EXCHANGE AND LEACHING IN SOILS

In one of the earliest attempts at modeling cation transfer through soils, Rible and Davis (1955) employed the chromatography theory of the De Vault (1943). Devault's theory applies to the flow of a solution containing an adsorbate through a column of absorbant, and it is based on material balance in each differential section in the column (i.e., the change in adsorbate content in each section is equal to inflow minus outflow from the section). The basic equation derived by De Vault is (Rible and Davis, 1955):

$$x = v/[a + Mf'(c)]$$

where x = depth in the column
v = volume of solution applied to the column
a = pore volume per unit length of column
m = amount of adsorbant per unit length of column
f(c) = adsorption isotherm of adsorbate to adsorbant
f'(c) = the first derivative of f(c) with respect to C.

The nature of the adsorption depends on the type of system being considered and the assumptions being made. For cation exchange involving two cations of the same valence, one could use a selectivity coefficient:

$$Q = \frac{(A)[Mg]}{(Mg)[Ca]}$$

where Q = the selectivity coefficient, parentheses denote exchangeable phase, and brackets denote solution phase.

Rible and Davis used a modification of this to account for ions of different valence also:

$$Q = \frac{(B_2)^{r_1}\,[B_1]^{r_2}\,([B_1] + [B_2])^{r_1 - r_2}}{(B_1)^{r_2}\,[B_2]^{r_1}}$$

where r_1 and r_2 are the valence of B_1 and B_2, respectively.

For exchange between cations of equal valence, this equation is the same as the one above. Any isotherm can be applied to the basic equation, but point-by-point equilibrium between solution and adsorbed phase is inherently assumed in this treatment.

The chromatographic equations of Hoister and Vermeulen (1952) allow for a finite rate of cation exchange rather than assuming point-by-point equilibrium, and Bower, et al. (1957) found good agreement between model output and experimental results from soil columns using this method.

Biggar and Nielsen (1963) show that neither the De Vault nor Hoister-and-Vermeulen equations are adequate for describing cation exchange during water flow through soils unless they account for miscible displacement, i.e., the effects of diffusion and variations in microscopic flow velocities on mixing and dispersion within the wetting front. Biggar, et al. (1966) later tested the finite plate method of modeling, which inherently introduces mixing within each soil section. The method is similar in principle to the chromatographic equations in that equilibrium is assumed and material balance is kept by adding inflow and subtracting outflow. The only difference is that the modeled soil is divided into finite plates of a certain thickness, and equilibrium solution is calculated for each plate, and this outflow from a given plate is added to the plate below, where a new equilibrium is calculated, etc.